07 States of Matter

Introduction:

For study of gases we require gas parameters like P, V, n and temperature. Gases having no interaction between gas molecules are known as ideal gases. They follow kinetic gas assumptions, kinetic gas equation, gas laws and ideal gas equation but certain gases which do not follow above conditions are known as real gases.

Graham's Law of Diffusion and Effusion:

(1) **Diffusion** is the process of spontaneous spreading and intermixing of gases to form homogenous mixture irrespective of force of gravity. While **Effusion** is the escape of gas molecules through a tiny hole such as pinhole in a balloon.

- All gases spontaneously diffuse into one another when they are brought into contact.
- Diffusion into a vacuum will take place much more rapidly than diffusion into another place.
- Both the rate of diffusion of a gas and its rate of effusion depend on its molar mass. Lighter gases diffuses faster than heavier gases. The gas with highest rate of diffusion is hydrogen.

(2) According to this law, "At constant pressure and temperature, the rate of diffusion or effusion of a gas is inversely proportional to the square root of its vapour density."

Thus, rate of diffusion $(r) \propto \frac{1}{\sqrt{d}}$ (T and P constant)

For two or more gases at constant pressure and temperature, $\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}}$

(3) Graham's law can be modified in a number of ways as,

(i) Since, 2 × vapour density (V.D.) = Molecular weight

then, $\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{d_2 \times 2}{d_1 \times 2}} = \sqrt{\frac{M_2}{M_1}}$

where, M_1 and M_2 are the molecular weights of the two gases.

(ii) Since, rate of diffusion $(r) = \frac{\text{Volume of a gas diffused}}{\text{Time taken for diffusion}}$

then, $\frac{r_1}{r_2} = \frac{V_1/t_1}{V_2/t_2} = \frac{w_1/t_1}{w_2/t_2} = \sqrt{\frac{d_2}{d_1}}$

(a) When equal volume of the two gases diffuse,

i.e. $V_1 = V_2$

then, $\frac{r_1}{r_2} = \frac{t_2}{t_1} = \sqrt{\frac{d_2}{d_1}}$

(b) When volumes of the two gases diffuse in the same time,

i.e. $t_1 = t_2$

then, $\frac{r_1}{r_2} = \frac{V_1}{V_2} = \sqrt{\frac{d_2}{d_1}}$

(iii) Since, $r \propto P$ (when P is not constant)

then, $\frac{r_1}{r_2} = \frac{P_1}{P_2}\sqrt{\frac{M_2}{M_1}} \quad \left(\because r \propto \frac{P}{\sqrt{M}}\right)$

(4) Rate of diffusion and effusion can be determined as,

(i) Rate of diffusion is equal to distance travelled by gas per unit time through a tube of uniform cross-section.

(ii) Number of moles effusing per unit time is also called as rate of diffusion.

(iii) Decrease in pressure of a cylinder per unit time is called as rate of effusion of gas.

(iv) The volume of gas effused through a given surface per unit time is also called as rate of effusion.

Real Gases:

Those gases which do not follow ideal gas equation (PV = nRT) at all temperature and pressure.

For real gases two assumptions of the kinetic theory do not hold good. These are

(i) There is no force of attraction between the molecules of a gas.

(ii) Volume of the molecules of a gas is negligibly small in comparison to the space occupied by the gas.

(a) Real Gas Equation or van der Waal Gas Equation

PV = nRT ...(1) ideal gas equation

Two major corrections are required for real gases

(i) The intermolecular force of attraction between molecules is not negligible.

$F_{att} \neq 0$ so $P_{act.} = \left(P_{real} + \frac{n^2a}{v^2}\right)$

(ii) The volume of a molecule is not negligible in comparison of total volume of gas.

$V_1 \neq 0$ so $V_{act} = (V - nb)$

b = covolume per mole = excluded volume = $4 \times \frac{4\pi r^3}{3} \times N_A$

From equation (i)

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

- a and b are Van der Waal's gas constants which depend on nature of gas but do not depend on the temperature and pressure.

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(A) van der Waal's gas constant (a) :

Where **a** is van der Waal gas constant which indicates the **inter molecular** forces of attraction.

$$\text{Pressure} = \frac{an^2}{V^2}$$

unit of **a** = atm L^2 mol^{-2}

$$P_i = P_R + \frac{an^2}{V^2}$$

$P_i > P_R$

- $a \uparrow$

  $\Rightarrow F_{att} \uparrow$

  $\Rightarrow$ liquefaction$\uparrow$
- Order of a is generally 10^{-1} to 10^{-2} atm L^2 mol^{-2}

(B) van der Waal gas constant (b)

It tells about molecular volume of gas molecules.

Unit of b = L mol^{-1}

b = incompressible volume

$V_i > V_R$

- If $b \uparrow \Rightarrow$ effective size of molecule$\uparrow$

  $\Rightarrow$ Incompressible volume $\uparrow$

  $\Rightarrow$ compressible volume $\downarrow$
- Order of b is generally 10^{-2} to 10^{-4} L mol^{-1}

(b) Deviation Of Real Gases From Ideal Gas Behaviour :

"At very low pressure and high temperature real gases behave as ideal gas." Deviation of real gases from ideal gas behaviour is mathematically denoted by "Z" named as **compressibility factor**.

$$Z = \frac{V_{real}}{V_{ideal}} = \frac{V_{obs}P}{nRT} = \frac{P(V_m)_{obs}}{RT}$$

Case I : If Z = 1; ideal gas; it signifies there is no interaction between gas molecules

$$\frac{P(V_m)_{obs}}{RT} = 1 \Rightarrow P(V_m)_{obs} = RT$$

Case II : If Z > 1; positive deviation from ideal gas behaviour; signifies repulsive forces are greater than attractive forces so such gases can't be liquefied easily.

$$\frac{P(V_m)_{obs}}{RT} > 1 \Rightarrow P(V_m)_{obs} > RT$$

The gas shows the positive deviation generally at high pressure from ideal gas behaviour.

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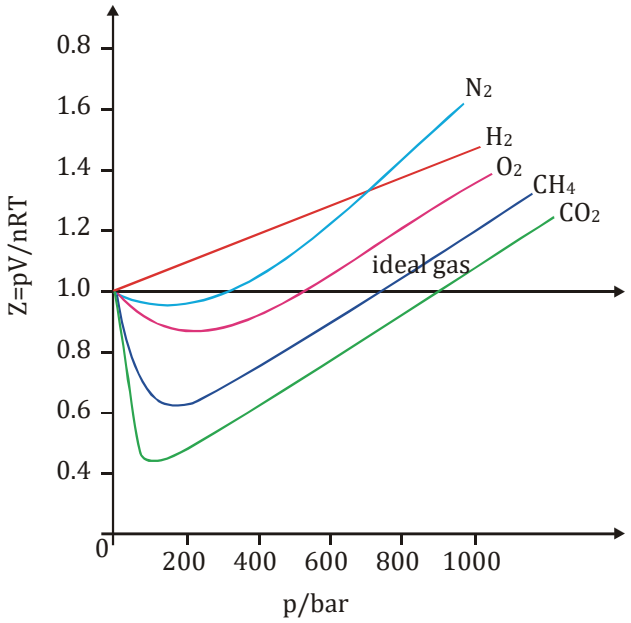
Case III : If Z < 1; Negative deviation from ideal gases behaviour; it signifies attractive forces are higher than repulsive forces so gas can be liquefied easily.

$$\frac{P(V_m)_{obs}}{RT} < 1 \Rightarrow P(V_m)_{obs} < RT$$

The gas show the negative deviation generally at low pressure from ideal gas behaviour.



(c) Effect of pressure on van der Waal gas equation

Case I : At very-very low pressure

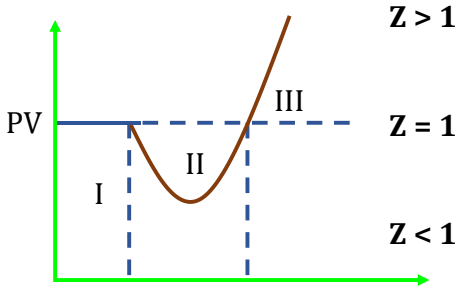
(Z = 1)

$$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT$$

$$PV = nRT$$

$$\frac{PV}{nRT} = 1$$

z = 1



Case II : At low pressure/moderate pressure

(Z < 1)

$$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT$$

$$PV + \frac{n^2a}{V} = nRT$$

$$\frac{PV}{nRT} + \frac{na}{VRT} = 1$$

$$\mathbf{Z = 1 - \frac{na}{VRT}}$$

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Case III : At very high pressure

(Z > 1)

$$\left(P+\frac{n^2a}{V^2}\right)(V-nb)=nRT$$

$PV - nPb = nRT$

$$\frac{PV}{nRT}+\frac{Pb}{RT}=1$$

$$\mathbf{Z=1+\frac{Pb}{RT}}$$

- At high temperature and low pressure, it acts as ideal gas equation.
- **Critical temperature (T_C) :** The temperature below which gas can be liquefied by application of pressure alone; is called critical temperature $\mathbf{T_c=\frac{8a}{27bR}}$.
- **Critical pressure (P_C) :** The pressure required to liquefy a gas at critical temperature; is called critical pressure.

$$\mathbf{P_c=\frac{a}{27b^2}}$$

- **Critical volume (V_C) :** Volume occupied by 1 mol gas at critical temperature & pressure; is called critical volume.

$\mathbf{V_c = 3b}$

- **Van Der waal gas constants :**

Gas	a (atm L^2 mol^{-2})	b (L mol^{-1})
H_2	0.244	0.0266
N_2	1.39	0.0391
CH_4	2.25	0.0428
CO_2	3.59	0.0427
NH_3	4.17	0.0371
H_2O	5.46	0.0305

- Higher value of **"a"** is more significant for liquefaction of a gas.
- **Boyle's Temperature (T_b) :** Temperature at which a real gas obeys ideal gas laws over an appreciable range of pressure is called Boyle's temperature.

$$\mathbf{T_b=\frac{a}{bR}}$$

Illustration 1:

The rate of effusion of a gas is proportional to

(1) $\frac{P}{\sqrt{d}}$ **(2)** $\frac{P}{d}$ **(3)** $\sqrt{\frac{P}{d}}$ **(4)** $\frac{\sqrt{P}}{d}$

Solution:

Ans. (1)

Rate of effusion $\propto \frac{1}{\sqrt{d}} \propto P$

$\therefore$ Rate of effusion $\propto \frac{P}{\sqrt{d}}$

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Illustration 2:

If 4g of oxygen diffuse through a very narrow hole, how much hydrogen would have diffused under identical conditions ?

(1) 16 g **(2) 1 g** **(3) 1/4 g** **(4) 64 g**

Solution:

Ans. (2)

$$\frac{V_{O_2}}{V_{H_2}};\frac{n_{O_2}}{n_{H_2}}=\sqrt{\frac{M_{w_{H_2}}}{M_{w_{O_2}}}}$$

$$\Rightarrow \frac{4/32}{w/2}=\sqrt{\frac{2}{32}}$$

$$\Rightarrow \frac{1}{4w}=\frac{1}{4}$$

$$\Rightarrow w=1$$

Illustration 3:

van der Waal's equation of state is obeyed by real gases. For n moles of a real gas, the expression will be

(1) $\left(\frac{P}{n}+\frac{na}{V^2}\right)\left(\frac{V}{n-b}\right)=RT$ **(2)** $\left(P+\frac{a}{V^2}\right)(V-b)=nRT$

(3) $\left(P+\frac{na}{V^2}\right)(nV-b)=nRT$ **(4)** $\left(P+\frac{n^2a}{V^2}\right)(V-nb)=nRT$

Solution:

Ans. (4)

Van der Waal's equation is $\left(P+\frac{n^2a}{V^2}\right)(V-nb)=nRT$

Illustration 4:

van der Waal's constant 'a' and 'b' are related with .....respectively –

(1) Attractive force and bond energy of molecules

(2) Volume and repulsive force of molecules

(3) Shape and repulsive forces of molecules

(4) Attractive force and volume of the molecules

Solution:

Ans. (4)

'a' is related to attractive forces and 'b' to the volume of the molecules.

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BEGINNER'S BOX-1

1. The rates of diffusion of SO_2 and O_2 are in the ratio –

(1) $1:\sqrt{2}$ (2) 1 : 32 (3) 1 : 2 (4) 1 : 4

2. In the van der Waal's equation which will have highest value of 'a'.

(1) CH_4 (2) He (3) NH_3 (4) H_2

3. The unit of the van der Waal's constant 'a' is :

(1) atm L^2 mol^{-2} (2) atm L^{-2} mol^{-2} (3) atm L mol^{-1} (4) atm mol L^{-1}

BEGINNER'S BOX ANSWERS KEY

BEGINNER'S BOX-1	Que.	1	2	3	
	Ans.	1	3	1	

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